1.0

4.5
5.0
5.6
6.3

2.8

2.5

1.1

3.2

3.6

4.0

2.2

2.0

1.8

1.25

1.4

1.6

MICROCOPY RESOLUTION TEST CHART
NATIONAL BUREAU OF STANDARDS-1963-A

The Reaction of Perfluoropolyalkylether Oil with FeF$_3$, AlF$_3$, and AlCl$_3$ at Elevated Temperatures

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1 April 1985

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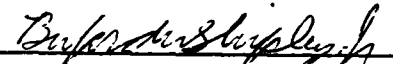DISTRIBUTION UNLIMITED

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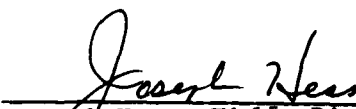Los Angeles, CA 90009-2960

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Bearings	Ketones	
Ferric fluoride	Lubricant degradation	
GPC	Perfluoropolyalkylether oil	

20. ABSTRACT *(Continue on reverse side if necessary and identify by block number)*
The interaction of perfluoropolyalkylether (PFPE) oil with ferric fluoride (FeF_3) and other Lewis acids at elevated temperatures under inert atmosphere was investigated to determine whether the reaction results in lubricant degradation. At 350°C, ~ 25°C below the onset of thermal degradation, PFPE's reaction with FeF_3 yields acyl fluoride and ketone degradation products and also a decrease in the oil's number average molecular weight.

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19. KEY WORDS (Continued)

20. ABSTRACT (Continued)

In the presence of small quantities of water, the acyl halide products hydrolyze, resulting in carboxylic acids. The oil's reaction with aluminum fluoride at 350°C and aluminum chloride at 200°C also causes it to degrade measurably. The results indicate that PFPE oil can degrade at estimated bearing asperity contact temperatures in the presence of FeF_3.

PREFACE

We thank Dr. P. D. Fleischauer for criticism of the manuscript.

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I. INTRODUCTION

Perfluoropolyalkylether (PFPE) oils (I) and oil-based greases are being used with increasing frequency in spacecraft systems because of their favorable properties, which include a wide application temperature range, good viscosity index, and general chemical inertness. The chemical inertness, however, must be evaluated in the light of extended satellite mission lifetimes and the rigors of operation in the orbital environment.

$$R_f \left(\!\! \begin{array}{c} CF\text{-}CF_2\text{-}O \\[2pt] | \\ CF_3 \end{array} \!\! \right)_{\!n} R_f'$$

(I)
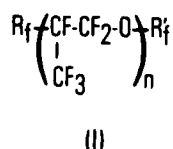
R_f and R_f' = perfluoropolyalkylether end groups of unspecified length; $n \approx 20$.

In studies performed in terrestrial environments, PFPE oils, although considered unreactive, have been observed to react under certain conditions. Under oxidizing conditions and in the presence of ferrous and titanium alloys at elevated temperatures (>260°C), PFPE oils degrade and cause metal to corrode by forming reactive degradation products.[1,2] When PFPE and other fluorinated ethers reacted with the Lewis acid aluminum chloride ($AlCl_3$) at moderate temperatures (~ 170°C), the resulting cleavage of the etherate linkage yielded ketone and acid halide degradation products.[3-5]

In our laboratories, tests of a PFPE-oil-based grease thickened with tetrafluoroethylene telomer were performed using 3.175 mm (1/8 in.) bore, 5R 2H, phenolic retainer miniature bearings; they were run at ambient temperature, 48.8 rpm, 22.25 N radial load, 11.12 N axial load, and ~ 8×10^{-7} Pa test pressure. After 5×10^6 revolutions, the bearings were disassembled and examined. Underneath a layer of tetrafluoroethylene telomer that had been burnished on the raceways, the raceway surfaces were extensively pitted,

indicating that chemical/physical degradation had occurred in the system. Auger analysis of the raceway surfaces revealed the presence of fluorine. Clearly, nonoxidative degradation of the grease had occurred.

Based on those observations, a mechanism was hypothesized to explain the lubricant degradation. The steps in the proposed mechanism are: 1) interaction between fluorocarbon and steel surfaces to form ferric fluoride (FeF_3) followed by 2) degradation of the PFPE oil through its reaction with the FeF_3 analogous to reactions of PFPE with $AlCl_3$. Step 1, interaction of fluorocarbon with iron leading to dehalogenation of the fluorocarbon, has been observed in systems in which aromatic products are formed, but has not been reported for aliphatic systems.[6] The aromaticity undoubtedly contributes in the reaction energetics by stabilizing both the transition state and the products. Whether FeF_3 was formed in these reactions was not reported; however, its formation is a likely possibility. The formation of metal fluoride compounds has been inferred in the reactions of PFPE oil with aluminum and ferrous alloys under oxygen-containing atmospheres[7] and titanium under oxygen and nitrogen.[8]

This report discusses one aspect of the PFPE-based lubricant-degradation mechanism: the reaction of PFPE oil with FeF_3.

II. EXPERIMENTAL

A. MATERIALS

The PFPE oil used was a hexafluoropropylene oxide polymer that was treated to remove the reactive end groups. The properties of the oil are listed in Table 1. The Lewis acids FeF_3, aluminum fluoride (AlF_3), and $AlCl_3$ were anhydrous and were used as received. The solvent was 1,1,2-trichloro-1,2,2-trifluoroethane (Freon TF) and was used as received.

B. EXPERIMENTAL REACTOR

The reactions of PFPE oil with Lewis acids were run in a recirculating autoclave system because of anticipated high reaction temperatures. Since reaction with ferrous alloys is a potential problem, a small, all-nickel-200 autoclave insert was fabricated (Fig. 1). PFPE fluids do not react significantly with nickel at the temperatures used in this study.[9] A nickel foil gasket or gold wire crush seal was inserted between the top and the base of the reactor to seal the system.

C. EXPERIMENTAL PROCEDURE

The experimental runs were begun by pipetting the oil into the nickel reactor. Dry nitrogen (N_2) gas was bubbled through the oil for more than 1 h to remove oxygen and water from the oil. While N_2 gas was passed over the surface of the reactor, the appropriate quantity of Lewis acid catalyst was added and the resulting slurry was stirred to achieve homogeneity. The reactor seal and lid were positioned and securely tightened. The nickel reactor was placed in the autoclave, and the appropriate thermocouples were attached. The autoclave was covered and sealed, then purged internally with dry N_2 gas at 207 to 276 kPa (30-40 psi). The gas pressure was maintained at >207 kPa (30 psi) during the course of the experimental runs. The autoclave was heated to the desired temperature and maintained at that temperature until the end of the run. After cooling, the autoclave was opened, and the nickel reactor was removed and opened. The slurry was centrifuged to remove the oil portion from the catalyst, and the remaining catalyst was extracted with Freon

TABLE 1. PERFLUOROPOLYALKYLETHER OIL PROPERTIES

Viscosity, cSt	
-18°C	6 900
38°C	85
Viscosity index	113
Pour point, °C	-43
Density, Mg·m^{-3}	
24°C	1.89
99°C	1.76
Approximate boiling range, °C at 107 Pa	227-251
Refractive index, n_D^{25}	1.300
Number average molecular weight	~3 700

o remove the remaining soluble oil and products. No capture of volatile

tion products was attempted, even though such products were clearly

ent in some of the runs. The experimental conditions are given in

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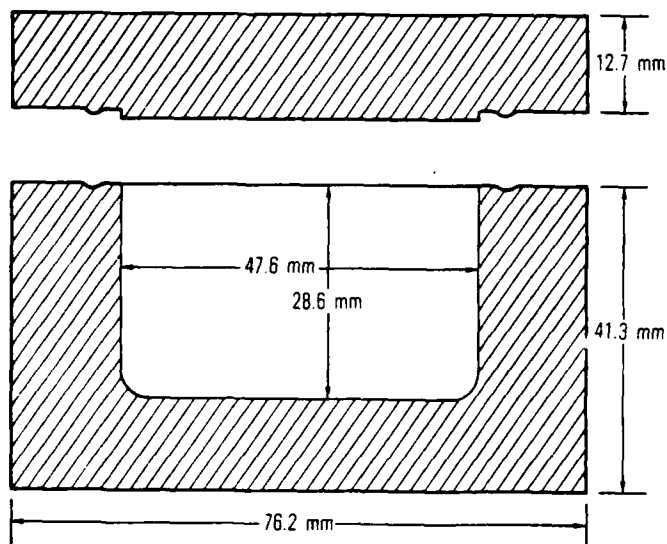
Fig. 1. Nickel 200 autoclave reactor insert.

INFRARED SPECTRAL ANALYSIS

The oil and oil-degradation products were examined spectrally using a
rier transform infrared spectrophotometer (FTIR). The samples were
lyzed neat, between salt plates. The data storage and manipulation capa-
ity of the FTIR system enabled the absorptions due to the unreacted oil to
subtracted and the small signals caused by the degradation products to be
¬ded.

¬OMATOGRAPHIC ANALYSIS

T₁ liquid products were analyzed by high-performance liquid chromato-
ph (HPLC) in the gel permeation chromatography (GPC) mode. The run
dit ons and instrument parameters were as follows: The columns, two 125 Å

:ive products, acyl halides, would react with the metal surfaces, thereby

asing the pitting of the surfaces and providing more sites for reac-

. The surface degradation could result in torque anomalies and increased

ing noise. The decrease in MW would result in decreased oil viscosity and

ased oil volatility, which would affect the properties of the lubricant

am as a function of reaction extent. In our 24 h tests at 350°C, approxi-

ly 10 to 15 percent of the oil was converted to lower MW in runs 4 and 10

'C) and 20 to 25 percent in runs 3 and 9 (Fig. 4)—substantial percen-

;. Further reaction would result in continued lowering of oil MW, with

dant changes in lubricity.

It is difficult to estimate the rate at which such changes would occur in

al bearing systems, since asperity contact temperatures and frequency of

icts are not well known for the various bearing materials. Also, the rate

depend on load, speed, surface finish, and other parameters. However,

ossibility that PFPE-oil-based lubricants can degrade must be considered

acecraft planners.
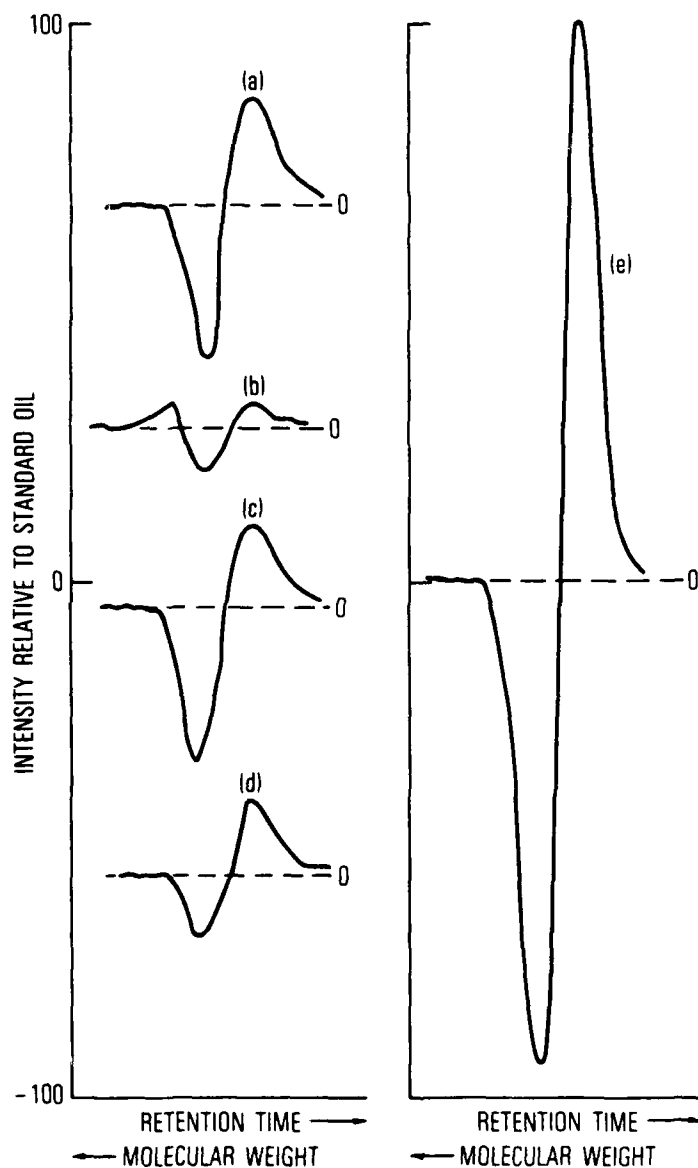
Fig. 4. GPC traces generated by subtracting the trace for the standard oil from the sample oil traces: (a) run 3, FeF_3, 350°C; (b) run 4, FeF_3, 350°C; (c) run 9, AlF_3, 350°C; (d) run 10, $AlCl_3$, 200°C; (e) run 5, FeF_3, 375°C.

ith considerable oil degradation. Both runs 9 and 10 exhibit broadening and
increases in lower MW components.

The GPC data were also treated by normalizing the areas under the peaks,
subtracting the standard peak from those of the samples of interest, and
plotting the difference against the retention time. The curves, presented in
Fig. 4 for runs 3, 4, 5, 9, and 10, indicate the extent of conversion of PFPE
to lower MW products. The negative, or downward-pointing, lobe is propor-
tional to the quantity of PFPE lost, whereas the positive, or upward-pointing,
lobe is proportional to increased quantities of lower MW materials. The
behavior of the curve for run 5 is the most extreme, indicating a complete
conversion of the original oil to degradation products. The curves for the
other runs show significant, but much smaller, effects.

The relative intensities of the infrared data, Fig. 2, do not appear to
correlate strongly with those of the GPC data, Fig. 4. The products in run 10
give strong IR bands but do not exhibit a large change in molecular weight.
One can only speculate that, at the lower temperatures in run 10, the cleavage
reactions are occurring at the ends of the polymer chains and, as a result,
there is not a substantial MW shift for the large fragments; whereas the lower
MW fragments are sufficiently volatile to be lost. For the other runs, 3
through 5 and 9, the higher temperatures may have resulted in more cleavage
toward the centers of the polymer chains, but more data are needed for
certainty. The infrared and gel permeation chromatography data clearly indi-
cate that reaction has occurred in runs 3, 4, 5, 9, and 10.

• IMPACT ON LUBRICATION

PFPE fluids are degraded in the presence of FeF_3 at elevated tempera-
tures. From an applications standpoint, this result signifies that, although
the degradation temperatures are high ($\sim 350°C$), they are still below that at
which thermal degradation occurs ($\sim 380°C$). Given that contact junction tem-
peratures have been estimated to be as high as 350°C,[23] lubricant degradation
could be system-life-limiting.

Oil degradation is manifested by the formation of chemically reactive
products and the lowering of the residual oil's molecular weight. The

TABLE 4. REACTION PRODUCT GPC DATA[*]

RUN NUMBER	PEAK MAXIMUM RETENTION TIME, min	PBV[†]	MOLECULAR WEIGHT AT A[‡]	MOLECULAR WEIGHT AT B[‡]
1	16.59	1.07	3672	2611
2	16.57	0.91	3715	2604
3	16.77	1.55	3309	2139
4	16.58	1.35	3693	2544
5	17.78	0.68	1846	1452
6	16.58	1.01	3693	2626
6A	16.59	1.00	3672	2596
7	16.58	1.03	3693	2596
8	16.59	1.03	3672	2596
9	16.68	1.44	3486	2313
10	16.59	1.58	3672	2374
Standard[§]	16.59	1.00	3672	2641

[*]Each value represents an average of two chromatograms of the same material. Variations were insignificant.
[†]PBV = peak broadening value (see text).
[‡]See Fig. 4.
[§]Unused oil.

The normalized values were then divided by the normalized value for the standard unused oil, resulting in a set of peak-broadening values (PBVs) that are internally normalized. The normalization operation is given by the following equation:

$$\text{Normalized PBV} = \frac{(\text{FWHM})_x}{\text{Height}_x} \div \frac{(\text{FWHM})_s}{\text{Height}_s}$$

where the subscripts x and s correspond to the sample of interest and the standard oil, respectively. The resulting normalized values are listed in Table 4.

The GPC traces can be quantitated by correlating retention time (RT) with MW. Regions in which the log MW is linear with RT for various GPC columns have been observed.[20-22] For the specific columns used in this study, the linear region of the plot is from MW ~ 20 000 down to ~ 1 000.[22] No suitable MW standards were available for the solvent and solute classes used, so a two-point calibration curve was constructed. The unreacted PFPE oil, investigated here, with a number average MW of ~ 3 700 (manufacturer's specification) and a different PFPE oil, a tetrafluoroethylene oxide polymer, with a number average MW of ~ 13 500 (manufacturer's specification) were used as the two standards. Because of batch-to-batch variations in the oils, those values are only approximate (good to ±10 percent) but serve as a guide so that trends can be established. The calibration curve is described by the following equation:

$$\log MW = -0.251RT + 7.729$$

The MW values for the points marked A and B in Fig. 3 were calculated using the above equation for each sample (see Table 4) and were used for comparison. The values listed for runs 1, 2, 6, 6A, 7, and 8 vary little relative to the value for the standard, unused oil. For run 3, the MW values indicate that there has been a shift to lower values as well as a broadening of the peak. Run 4 exhibits some broadening with a slight MW decrease at point B. The run 5 data exhibit a large MW shift. Although the peak is narrower than the standard's, the MW has shifted to much lower values, consistent

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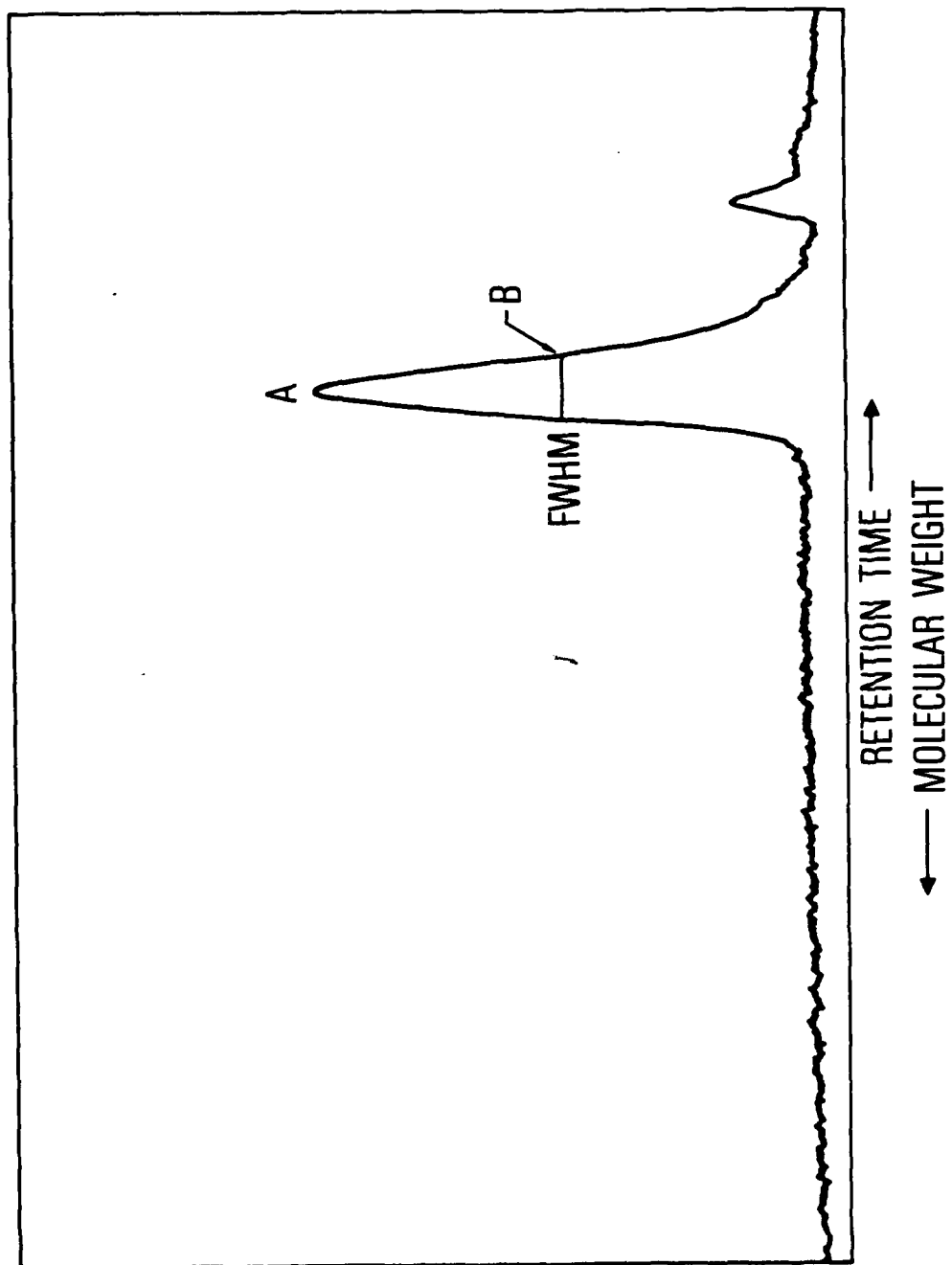
Fig. 3. Typical GPC trace: point A is at curve maximum, point B is at FWHM point (see text).

The IR spectrum for run 10 is the most complex of the five spectra. Absorption bands occur at 1806, 1878, and 1886 cm^{-1}, consistent with the fluorinated acyl fluoride and ketone that were observed in run 3. In addition, there are significant bands at 1789 and 1818 cm^{-1}, corresponding to acyl chloride products. CF_3COCl absorbs at 1810 cm^{-1} in the vapor phase[15] and at 1799 cm^{-1} in the condensed phase.[16] Multiple absorbances would more than likely occur for the acyl chloride products.[12,13]

The observation that absorption bands can be assigned to (II), (III), and acyl chloride in run 10 implies that halide exchange prior to cleavage is not facile. If halide exchange were facile with PFPE, a number of different fluorine- and chlorine-substituted products would be expected that would be spectrally distinguishable. Chlorine substitution would not be favored because fluorine substituents α to the ether oxygen destabilize the oxonium ion intermediate less than chlorine and would facilitate cleavage. The σ^+ values for halide substitution indicate that fluorine provides more stabilization of incipient carbonium ions than do the other halides when direct resonance interaction with the positive carbon is possible.[17,18] The acyl fluorides and acyl chlorides may be the result of halide exchange in the acyl halides. Rapid exchange has been reported for the $C_6H_5COCl + Al\ (^{36}Cl)_3$ system.[19]

B.   GEL PERMEATION CHROMATOGRAPHY

Figure 3 shows a typical GPC trace. In GPC, the movement of sample molecules is retarded by the packing material, so that the sample components are eluted from the column in order of decreasing molecular size [which is approximately proportional to molecular weight (MW)]; i.e., the lower MW material is on the right in Fig. 3. Changes in the GPC traces as a function of reaction are observed in the retention times of the peak maxima and broadening of the peaks as higher MW materials are depleted and lower MW materials are formed.

The retention time is available directly from the GPC trace; however, the trace broadening is more subtle. Borrowing from spectroscopy, we can use the full width at half maximum (FWHM) as a measure of GPC trace broadening. The FWHM of each trace was divided by the peak height to normalize the broadening.

The IR spectra for runs 4 and 5, aside from one major absorption band in each spectrum, are very similar. Small, unassigned absorption bands appear at 1722 and 1737 cm^{-1}; absorptions that correspond to carboxylic acids appear at 1752 and 1777 cm^{-1}; and slight absorptions appear at 1806, 1878, and 1886 cm^{-1}, indicating the possible presence of (II) and (III). The spectral similarities can probably be attributed to the reaction temperatures: For run 5, the reaction temperature was maintained at 375°C; the temperature during run 4, although nominally set at 350°C, exceeded 365°C for several hours.

At higher temperature, thermal degradation can become the predominant pathway. The thermal degradation of PFPE at 380°C under inert atmosphere has yielded CF_3COF and COF_2, and other products.[1] The hydrolysis of those products, as well as the hydrolysis of the products from the catalyzed ether cleavage pathway, could cause the strong absorption band at 1766 cm^{-1} and the bands at 1766 and 1777 cm^{-1} in the run 5 spectrum. [Significant amounts of water were detected in the run 5 products, whereas one-fourth as much water was detected in the run 4 products. Since it is unreasonable for water to form during the reactions, it must enter during the analytical workup.] Fluorinated carboxylic acids have absorption bands in that spectral region.[13] In contrast, the run 4 spectrum has a strong band at 2052 cm^{-1}, which could be assigned to an ion pair such as FeF_4^- $[R_fCO^+]$. In the reaction of $AlCl_3$ with CH_3COCl, absorption at 2193 cm^{-1} has been assigned to the acylium ion of the ion pair $AlCl_4^-$ $[CH_3CO^+]$.[14] Another possibility is a ketene, $(R_f)_2C=C=O$. The species responsible for the 2052 cm^{-1} absorption can only be speculated at this juncture, however.

The significant IR absorptions for run 9 occur at 1777 and 3618 cm^{-1}, and have been assigned to fluorinated carboxylic acids[13] and water, respectively. A slight absorption occurs in the spectral region where the fluorinated ketone (III) absorbs. As in run 5, a significant amount of water is present in the products, which would be consistent with hydrolysis of acyl fluorides to form carboxylic acids. That substantial amounts of ketone are lacking in the products of the reaction with the AlF_3 catalyst indicates that there may be some selectivity in the cleavage reaction that depends on the nature of the catalyst.

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The reaction products, acyl fluoride (II) and ketone (III), are those expected for the catalyst-assisted cleavage of the etherate carbon-oxygen bond (the mechanism is depicted in the accompanying Scheme). That both (II) and (III) were observed implies that cleavage occurs at both the primary carbon-oxygen bond to form ketone (route B) and at the secondary carbon-oxygen bond to produce acyl fluoride (route A). Van Dyke Tiers[3,4] reported that, in the reactions of (IV) with $AlCl_3$, cleavage occurred only at the secondary carbon-oxygen bond to form the acyl chloride (V). [Chlorine-fluorine exchange occurred at the α- carbons prior to cleavage.[3,4]] Our results clearly indicate that cleavage can occur in both places.

SCHEME

R_f-CF(CF$_2$)$_2$CF$_2$ $\xrightarrow{\quad AlCl_3 \quad}$ R_fCCl$_2$(CF$_2$)$_2$COCl

(IV)   (V)

TABLE 3. INFRARED ABSORPTION-BAND ASSIGNMENTS

RUN NUMBER	ABSORPTION BAND, cm^{-1}	INTENSITY, % Transmittance	ASSIGNMENT[*]
3	1806	2	$R_f-O-CF_2-COCF_3$
	1878	1	$R_f-O-CF(CF_3)COF$
	1886	1	
	3618	1	H_2O
4	1722	<1	No assignment
	1737	<1	
	2050	2	FeF_4^- $[R_fCO^+]$
	3618	2	H_2O
5	1722	1	No assignment
	1737	1	
	1752	shoulder	
	1766	6	R_fCF_2COOH
	1777	shoulder	
	3618	8	H_2O
9	1777	1.5	R_fCF_2COOH
	3618	3	H_2O
10	1789	1	$R_f-O-CF(CF_3)COCl$
	1806	8	$R_f-O-CF_2COCF_3$
	1818	8	$R_f-O-CF(CF_3)COCl$
	1878	1	$R_f-O-CF(CF_3)COF$
	1886	1	
	3618	1	H_2O

[*]See text.
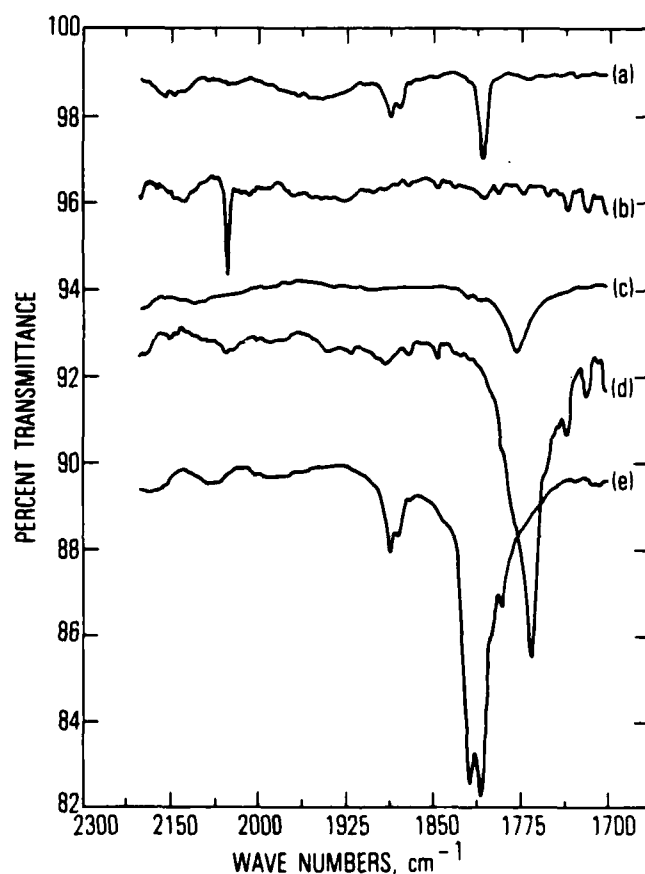
Fig. 2. FTIR spectra of the reaction products of perfluoropolyalkylether with Lewis acid catalysts: (a) run 3, FeF_3, 350°C; (b) run 4, FeF_3, 350°C; (c) run 9, AlF_3, 350°C; (d) run 5, FeF_3, 375°C; (e) run 10, $AlCl_3$, 200°C.

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III. RESULTS AND DISCUSSION

A. INFRARED SPECTROSCOPY

The background-subtracted infrared (IR) spectra of the liquid products for runs 3, 4, 5, 9, and 10 are depicted in Fig. 2 and their assignments listed in Table 3. (The IR spectra of the products of runs 1, 2, 6, 6A, 7, and 8 did not exhibit significant degradation-product absorption bands.) Only the 1700 to 2200 cm^{-1} region is shown because the absorption bands of interest occur primarily in that spectral region, except for an absorption band at 3618 cm^{-1} that was present in the spectra of all the samples.

The significant spectral bands are of low intensity, indicating that the functional groups responsible for the absorption bands are present in much lower concentrations than the perfluoropolyalkylether functionalities in the product oil. This result is consistent with 1) low levels of reaction or 2) the products being significantly volatile. The first reason is more likely, since very little material was lost in the experimental runs; i.e., less than 10 percent of the oil was lost during reaction.

The spectrum for run 3 exhibits a doublet at 1878 and 1886 cm^{-1} that has been assigned to R_f-O-CF(CF$_3$)COF (II). Fluorinated acid fluorides absorb in that spectral region (CF$_3$COF, 1905 cm^{-1}, and CF$_3$CF$_2$COF, 1890 cm^{-1}).[10] The absorption band at 1806 cm^{-1} can be assigned to R_f-O-CF$_2$CO-CF$_3$ (III) by analogy to CF$_3$COCF$_3$, 1809 cm^{-1}.[11] The 3618 cm^{-1} absorption band most likely reflects the presence of water in the products. The acid fluoride absorption appears as a doublet, 1878 and 1886 cm^{-1}. α- halogen substitution has been reported to cause multiple carbonyl absorptions because of conformational isomers,[12,13] or Fermi resonance.[12] The only other possible products that might effect the observed IR spectrum are fluorinated anhydrides—a possibility that can be eliminated because the formation of anhydrides requires the presence of carboxylic acids created from hydrolysis of the acid fluorides (and also the anhydrides). In run 3, no spectral evidence for carboxylic acids was detected.

μ-Bondagel porous silica columns with ether functionalities that had been bonded to the surface of the solid phase, were 30 cm long and 0.4 cm in diameter and were connected in series. The solvent was Freon TF at a flow rate of 0.3 mL/min. The sample size was 20 μL of an approximately 2 weight percent solution administered using a fixed-volume injection loop. A refractive index (RI) detector was used to analyze the column effluent.

TABLE 2. SAMPLE TEST CONDITIONS

RUN NUMBER*	CATALYST	CATALYST WEIGHT, g	MOLE RATIO[†]	TEMPERATURE, °C	TIME, h
1	FeF_3	10	0.80	250	24
2	FeF_3	2	0.16	300	24
3	FeF_3	2	0.16	350	24
4	FeF_3	4	0.16	350[‡]	120
5[§]	FeF_3	2	0.16	375	24
6[ǁ]	–	–	–	350	24
6A[#]	–	–	–	350	24
7	AlF_3	2	0.22	150	56
8	AlF_3	2	0.22	250	24
9	AlF_3	2	0.22	350	24
10	$AlCl_3$	2	0.14	200	24

*10 cm^3 or 18.6 g of perfluoropolyalkylether used in each run except run 4, in which 20 cm^3 of oil was used.
[†]Moles catalyst/moles perfluoropolyalkylether oil.
[‡]Reaction temperature exceeded 365°C for several hours.
[§]Reaction vessel leaked.
[ǁ]Oil without catalyst.
[#]Oil without catalyst in previously unused reaction vessel.

IV. CONCLUSIONS

Based on our experimental results, the following conclusions can be drawn:

1. FeF_3 catalysis of the degradation of PFPE can occur at temperatures below those for the onset of thermal degradation.

2. Degradation can cause changes in the PFPE that can ultimately affect the lubricity and lifetime of the lubricant.

3. The catalyzed degradation involves etherate cleavage at both primary and secondary carbons, resulting in acyl halide and ketone degradation products as well as perfluorinated ether products of reduced molecular weight.

The formation of FeF_3 in catalytic amounts is one of the key steps in our proposed oil-degradation mechanism. Whether FeF_3 is formed in significant quantities in bearing systems is uncertain, although there were indications it was present in our bearing tests. We plan to verify its formation in future experiments.

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LABORATORY OPERATIONS

The Laboratory Operations of The Aerospace Corporation is conducting experimental and theoretical investigations necessary for the evaluation and application of scientific advances to new military space systems. Versatility and flexibility have been developed to a high degree by the laboratory personnel in dealing with the many problems encountered in the nation's rapidly developing space systems. Expertise in the latest scientific developments is vital to the accomplishment of tasks related to these problems. The laboratories that contribute to this research are:

Aerophysics Laboratory: Launch vehicle and reentry fluid mechanics, heat transfer and flight dynamics; chemical and electric propulsion, propellant chemistry, environmental hazards, trace detection; spacecraft structural mechanics, contamination, thermal and structural control; high temperature thermomechanics, gas kinetics and radiation; cw and pulsed laser development including chemical kinetics, spectroscopy, optical resonators, beam control, atmospheric propagation, laser effects and countermeasures.

Chemistry and Physics Laboratory: Atmospheric chemical reactions, atmospheric optics, light scattering, state-specific chemical reactions and radiation transport in rocket plumes, applied laser spectroscopy, laser chemistry, laser optoelectronics, solar cell physics, battery electrochemistry, space vacuum and radiation effects on materials, lubrication and surface phenomena, thermionic emission, photosensitive materials and detectors, atomic frequency standards, and environmental chemistry.

Computer Science Laboratory: Program verification, program translation, performance-sensitive system design, distributed architectures for spaceborne computers, fault-tolerant computer systems, artificial intelligence and microelectronics applications.

Electronics Research Laboratory: Microelectronics, GaAs low noise and power devices, semiconductor lasers, electromagnetic and optical propagation phenomena, quantum electronics, laser communications, lidar, and electro-optics; communication sciences, applied electronics, semiconductor crystal and device physics, radiometric imaging; millimeter wave, microwave technology, and RF systems research.

Materials Sciences Laboratory: Development of new materials: metal matrix composites, polymers, and new forms of carbon; nondestructive evaluation, component failure analysis and reliability; fracture mechanics and stress corrosion; analysis and evaluation of materials at cryogenic and elevated temperatures as well as in space and enemy-induced environments.

Space Sciences Laboratory: Magnetospheric, auroral and cosmic ray physics, wave-particle interactions, magnetospheric plasma waves; atmospheric and ionospheric physics, density and composition of the upper atmosphere, remote sensing using atmospheric radiation; solar physics, infrared astronomy, infrared signature analysis; effects of solar activity, magnetic storms and nuclear explosions on the earth's atmosphere, ionosphere and magnetosphere; effects of electromagnetic and particulate radiations on space systems; space instrumentation.

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